



Surface Specific Spectroscopy of Polymers Developed *Structure of Polymer Chains Observed*

An MSD team led by Gabor Somorjai and Y. Ron Shen have, for the first time, generated surface-specific vibrational spectra from polymers. The results confirm that polymer “end groups” can segregate to the surface, where they affect key performance parameters.

Many of the chemical and mechanical properties of polymers, such as wettability, friction, lubricity, wearability, chemical reactivity, biological compatibility, permeability, charge storage capacity, and electrical response, can be correlated with the molecular structure and composition of the polymer surface. To control surface properties by manipulating the surface structure, one must have an extensive understanding of the detailed correlations between the properties and the structure of the polymer. However, very little work has been reported on such structure-property correlations due to the absence of techniques capable of studying polymer surface structure. Ideally, these techniques must be sensitive to molecular features such as conformational structure and hydrogen bonding. Various spectroscopic techniques, such as reflection infrared spectroscopy and Raman spectroscopy have been used in these studies, but they lack true surface specificity. Contact angle measurement, neutron reflection, and X-ray photoelectron spectroscopy are surface sensitive, but they often do not provide structural information and/or do not allow measurements under *in-situ* conditions such as in aqueous solution.

Over the past few years, Shen and Somorjai have developed infrared and visible sum-frequency generation (SFG) vibrational spectroscopy as a surface-specific spectroscopic tool having monolayer sensitivity (Highlight 96-9) and have applied it to studies of ice and catalytic metal surfaces monitored during reactions (Highlight 99-5). SFG retains the advantages of laser techniques, namely, it is nondestructive, highly sensitive, and has good spatial, temporal, and spectral resolution. Thus, when applied to *in situ* surface science, it is powerful and versatile and not only permits identification of surface molecular species but also provides information about orientation of functional groups at the surface.

It is known that the “end groups” of polymer chains can have a disproportionately large effect on the surface properties of the polymer. It has long been thought that under some conditions these groups preferentially segregate to the polymer surface due to their greater mobility relative to the backbone of the polymer chain. The MSD team put this long-standing assumption to the test in a series of polyurethane-based biopolymers (BioSpan series, The Polymer Technology Group, Inc.). In these polymers, the hydrophobic and hydrophilic end groups are being used to attempt to tailor the surface to, for example, discourage blood coagulation while retaining the good mechanical properties of the polymer backbone. This approach only works, of course, if the endgroups are actually found at the surface. Surface-specific vibrational spectra (see figure) provided a clear identification of the species located at the polymer surface. It was observed that hydrophobic end groups tended to segregate to the surface in air where they could therefore control the surface properties. In contrast, hydrophilic end groups were buried; their vibrational signatures were not observed at the surface.

The team is working to extend this work to determine changes in surface structure produced by environmental changes (e.g. air vs. water in contact with the surface) and by interactions with biological molecules.

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Z. Chen, R. Ward, Y. Tian, S. Baldelli, A. Opdahl, Y.-R. Shen, and G. A. Somorjai, “Detection of hydrophobic end groups on polymer surfaces by sum-frequency generation vibrational spectroscopy,” *J. Amer. Chem. Soc.*, 122, (43), 10615-10620 (2000).